

PATENT SPECIFICATION

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(54) A PROCESS FOR FILM FORMATION

- (71) We, MITSUBISHI RAYON COMPANY, LTD., a corporation organ-
 ised under the laws of Japan, of 2—8, Kyobashi, Chuo-ku, Tokyo, Japan, do hereby
 declare the invention for which we pray that a patent may be granted to us, and the
 method by which it is to be performed, to be particularly described in and by the
 following statement: —
 This invention concerns a process for providing a coating on a base material,
 which coating adheres well to the base material and has good anti-corrosion properties.
 Heretofore, a base material, particularly a metal base such as steel or aluminum
 plates, is treated chemically in order to improve its anti-corrosion properties, its ability
 to accept a coating and its post-processability. The chemical treatment is effected with
 chemicals such as phosphates and chromates or with Al_2O_3 -film formation. However,
 this treatment is not entirely satisfactory.
 According to the present invention there is provided a process for forming a coat-
 ing film, which comprises pre-coating the surface of a base material with a first coat-
 ing material (I) containing 1 to 85 weight % of free isocyanate groups, then coating
 thereon a second coating material (II) comprising a compound having 0.5 to 12 poly-
 merizable unsaturated groups per 1000 molecular weight units and hardening by cross-
 linking the thus prepared coating film by irradiation with ionizing radiation and/or
 ultraviolet ray radiation.
 Coating material (I)
 Isocyanate compounds suitable for use in the practice of the present invention,
 include such aliphatic or aromatic monoisocyanates as butylisocyanate, laurylisocyanate,
 octadecylisocyanate and phenylisocyanate. Also suitable are diisocyanates of the for-
 mula $OCN-R-NCO$ wherein R is an alkyl group having from 2 to 36 carbon atoms
 or a cyclohexyl group. Examples include tetramethylenediisocyanate, hexamethylenedi-
 isocyanate, lysine diisocyanate, dimer acid diisocyanate and cyclohexane diisocyanate;
 and aromatic diisocyanates such as tolylenediisocyanate, xylylenediisocyanate, diphenyl-
 methanediisocyanate, m-phenylenediisocyanate and bisphenylene diisocyanate.
 Furthermore, there may be used products obtained by reacting or partially
 reacting the aforesaid isocyanates with aliphatic, aromatic or alicyclic compounds having
 one active hydrogen atom, e.g. a hydroxyl group, an amino group or a carboxyl group.
 Such products must contain from 1 to 85 weight % of free isocyanate groups. Examples
 of said products include those obtained by reacting such polyisocyanate compounds
 as tolylenediisocyanate, xylylenediisocyanate or hexamethylenediisocyanate, with at least
 one of ethanol, butanol, lauryl alcohol, phenol, laurylamine, octylamine, acetic acid,
 propionic acid, stearic acid and benzoic acid.

Furthermore, the coating material (I) may also comprise addition reaction products of the aforementioned isocyanates with compounds having two or more functional hydrogen atoms in the molecule, e.g. water, ethylene glycol, glycerine, trimethylolpropane, pentaerythritol, hexamethylenediamine, ethylenediamine, ethanolamine, phthalic acid, succinic acid, adipic acid, sebacic acid, trimellitic acid, polyesters obtained from polyhydric alcohol and polycarboxylic acid, polyesters having hydroxyl groups on the side chain, vinyl polymers having vinyl groups on the side chain, and polyamides obtained from polyamines and polycarboxylic acids or amino acids. Only those products containing from 1 to 85 weight % of free isocyanate groups are suitable for use in the present invention. Examples of such products include a polyisocyanate (trade name, Desmodur N—75) obtained by reacting 3 moles of hexamethylenediisocyanate with 1 mole of water; a polyisocyanate (trade name, Desmodur L—75) obtained by reacting 3 moles of tolylenediisocyanate with 1 mole of trimethylolpropane; a polyisocyanate (trade name Takenate D—110N) obtained from xylylenediisocyanate and trimethylolpropane; and a partial addition product of hexamethylenediisocyanate and polyester. The words "Desmodur" and "Takenate" are Registered Trade Marks.

In the present invention, the coating material (I) is desirably used in combination with additives such as organic solvents, organic resins, pigments or fillers, which are not excessively reactive with the isocyanate groups contained in the coating material (I). The coating material (I) thus prepared has good coating processability and is easy to handle.

The aforementioned organic solvents include ketone type solvents such as acetone, methyl ethyl ketone and methylisobutyl ketone, and ester type solvents such as ethyl acetate and butyl acetate, and aromatic solvents such as toluene and xylene. Suitable organic resins include cellulose derivatives such as nitrocellulose and cellulose acetate butyrate, epoxy resins, vinyl polymers, polyesters, polyamides, epoxylated 1,2-polybutadiene, chlorinated rubber and chlorosulfonated polyethylene. Organic or inorganic pigments may be used in this invention. The pigments are preferably those used for rust prevention, such as zinc chromate, strontium chromate, iron oxide, zinc oxide, zinc powder, aluminium powder, lead-iron alloy powder and barium metaborate. Pigments are preferably used in amounts of from 5 to 300 parts by weight based on 100 parts by weight of the coating material (I).

The coating material (I) is usually applied in an amount so that the film formed is in the dry state from 0.01 to 5 μ thick.

The coated layer, which is coated on the base material with the coating material (I), can be dried by heating at a temperature of from 15° C to 450° C, preferably 50° C to 350° C. Drying will normally be carried out in a blown gas stream. The gas can be air, nitrogen, carbon dioxide, steam, argon or a mixture thereof.

The most preferred material for the coating material (I) is the product obtained by partially reacting A and B mentioned below.

A: compounds having two or more isocyanate groups in a molecule.

B: hydroxyl compounds selected from B—1, B—2, B—3, B—4 and B—5.

B—1: butyral resin where butyralization degree is 40 mol % or more and concentration of vinyl alcohol is 60 mol % or less.

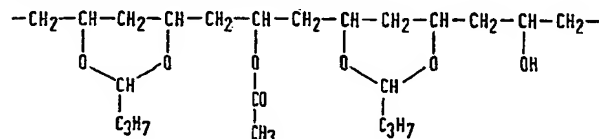
B—2: polyester (molecular weight 300—5000; hydroxyl value: 20—350), obtained from polycarboxylic acids and polyhydric alcohols containing at least 30 mol % of aliphatic polyhydric alcohols.

B—3: acrylic copolymer (molecular weight 1,000—100,000; hydroxyl value 20—300) containing 20% by weight or more of acrylate.

B—4: polyether (hydroxyl value 20—500) containing 2 or more ether-linkage in a molecule.

B—5: 1,2-polybutadiene (molecular weight 300—100,000; hydroxyl value 30—500)

The above B—1 has the following structure:



which has vinyl butyral, vinyl acetate and vinyl alcohol units. The degree of acetylation is preferably 30 mol % or more, and the viscosity (Ostwald) is preferably 5—600

centi-poise in a 10% solution of ethanol-toluene (1:1) at 20° C (which corresponds to polymerization degree of 200—2,000). If the degree of butyralization is less than 40 mol % and vinyl alcohol unit is more than 60%, the butyral resin does not dissolve in the solvent for the isocyanate and not provide a good primer.

With respect to B—2, the polycarboxylic acid moiety can be malonic acid, oxalic acid, succinic acid, maleic acid, fumaric acid, glutaric acid, itaconic acid, adipic acid, sebacic acid, diglycolic acid, phthalic acid, isophthalic acid, terephthalic acid, dimethyl-terephthalic acid, tetrahydrophthalic acid, tetrabromophthalic acid, hexahydrophthalic acid, naphthalenedicarboxylic acid, endomethylene tetrahydrophthalic acid, p-carboxyphenyl acetic acid, or benzophenone 4,4'-dicarboxylic acid phenyl di-β-carboxyethylamine.

The aliphatic polyhydric alcohol, the other moiety, can be ethylene glycol, propylene glycol, 1,3-buteneglycol, 1,4-cyclohexane diol, diethyleneglycol, neopentylglycol, hexamethyleneglycol, glycerine, trimethylolpropane, pentaerythritol, polyalkyleneglycol having 1—10 ether linkages in glucose molecule such as polyethylene glycol, polypropyleneglycol, polytetrahydrofuran and polyethyleneoxide copolymer glycol. Alternatively, it can be bisphenol A, p-dihydroxymethylbenzene, hexahydroresorcinol, or hydroquinone. The aliphatic components in the polyhydric alcohols affords flexibility to the film and easily produce radicals when irradiated. The final coating adheres well to the primer obtained from B—2.

Preferably, the polybasic alcohol component will contain at least 30 mol % of an aliphatic component. Molecular weight can be 300—5,000, preferably, 400—2,000, when high solubility in the solvent for the isocyanate and processability of the film are required. Hydroxyl value of the polyester should be 20—350 mg KOH/g. As this value increases, the reactivity with isocyanate increases, but water resistance and flexibility of the primer coating decreases. 50—200 is preferred.

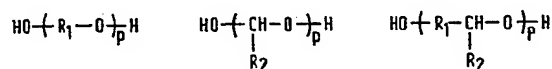
Regarding B—3, it can be prepared from acrylic acid, methacrylic acid, itaconic acid, acrylates, vinyl monomers containing hydroxyl groups, aromatic monovinyl compounds, ethylenically unsaturated nitriles or monovinyl esters of organic acids. The acrylates serve to improve flexibility of the film and increase cross-linking in the primer to provide a tough film, because the acrylate is easily cross-linked upon irradiation. The polymer preferably has a molecular weight of from 1,000 to 100,000.

The vinyl monomers having hydroxyl groups are preferably acrylate, methacrylate, itaconate, glutaronates or maleates wherein the hydroxyl groups are 2-hydroxyethyl, 2-hydroxypropyl, 4-hydroxybutyl, or 6-hydroxyhexyl; allyl alcohol, methallyl alcohol, and hydroxyalkylacrylamide or methacrylamide.

These monomers are preferably used so that hydroxyl value of the copolymer is within the range from 20 to 300.

Comonomers include acrylic acid, methacrylic acid, itaconic acid, acrylates or methacrylates obtained by ester exchange between methacrylic acid and alcohols having alkyl groups of from 1 to 2 carbon atoms, cyclohexyl alcohol, phenyl alcohol, benzyl alcohol or phenethyl alcohols. Alternatively, they may be aromatic vinyl compounds such as styrene or vinyl toluene; nitriles such as acrylonitrile or methacrylonitrile; vinyl esters such as vinyl acetate or vinyl propionate; acrylamide, methacrylamide and N-butoxymethyl acrylamide or methacrylamide.

As to B—4, they have the following formulae:



wherein:

R₁: aliphatic, aromatic or alicyclic groups such as methylene, ethylene, propylene, butylene, benzene, cyclohexane or paraxylene,

R₂: H or lower alkyl groups such as CH₃, and

p: integer from 2—100.

Examples include polyethers obtained from polymerizing or copolymerizing substituted or unsubstituted cyclic ethers such as ethylene oxide, propylene oxide, tetrahydrofuran, and oxacyclobutane. Further examples are polyethers obtained by reacting the following (a) and (b):

(a) glycerine, trimethylolpropane, triethylolpropane, hexanetriol, pentaerythritol, sorbit, sucrose, propylenethioglycol, diethylenethioglycol or ethylenediamine;

(b) Substituted or unsubstituted cyclic ethers.

The hydroxyl value is preferably from 50 to 200.

In connection with B—5, the polybutadiene has hydroxyl group at the terminal or in the side chain. The latter can be obtained by reaching epoxylated 1,2-polybutadiene with monohydric or polyhydric alcohols or monovalent carboxylic acids. Preferable hydroxyl value is 50—300 from the points of reactivity and flexibility.

The coating material (I) is preferably prepared in the presence of catalysts such as organic amines or organometallic compounds. Primary or secondary amines are not normally preferred, because they react with the isocyanate moiety to make it inactive. Tertiary amines, which are preferred, include triethanol amine, triethylamine, N,N,N',N'-tetramethyl 1,3-butanedi-amine, dimethylethanolamine, bisdiethylethanolamine adipate, N-methyl morpholine, N-(2-hydroxypropyl) dimethyl morpholine, dimethyl aminoethyl acrylate or methacrylate, 2-vinylpyridine, 3-ethyl-5-vinyl-pyridine, dimethyl acrylamide or methacrylamide, dimethylaniline and N,N-bis-(2-hydroxypropyl)-2-methyl piperazine. Particularly preferred are tertiary amines which have a hydroxyl group, because they can react with the isocyanate moiety to produce a film-forming component as well as acting as a catalyst. Organometallic catalysts include dibutyl tin dilaurate dibutyl tin di(2-ethylhexoate), stannous 2-ethylcaproate and stannic chloride.

These catalysts are normally used in an amount of 40 parts by weight or less per 100 parts by weight of the total of (A) and (B) moieties. Preferably the first coating material (I) is dried after application to the base material until it contains at least 10% by weight of an insoluble portion (measured in acetone at 25° C). Drying may be effected by blowing gas at a temperature from room temperature to 300° C on to the coated surface.

Coating material (II)

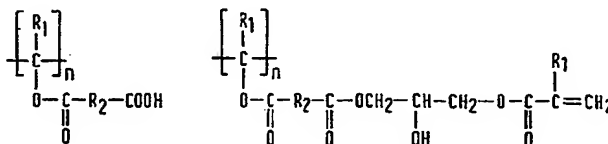
The coating material (II) to be cross-linked by irradiation is a composition principally consisting of compounds having from 0.5 to 12 of polymerizable unsaturated groups per 1000 of molecular weight. If there are less than 0.5 unsaturated groups, cross-linkage formation is not good even after irradiation, while when there are more than 12 unsaturated groups, flexibility and impact strength of the film tend to be reduced.

Typical examples are:

(1) a composition consisting of unsaturated polyesters with or without vinyl monomers; said polyester being prepared from polyvalent carboxylic acids mainly composed of α,β -unsaturated carboxylic acids such as maleic acid and itaconic acid, and polyhydric alcohols,

(2) a composition mainly consisting of polymers having polymerizable unsaturated groups in the side chain;

(2—1): a composition consisting of modified polymers having hydroxyl groups in the side chain defined below with or without vinyl monomers; said polymers being polyesters having hydroxyl groups in the side chain or polymers mainly composed of hydroxyl group-containing vinyl monomers, which are modified with polymerizable carboxylic acid anhydrides or further modified with glycidyl group-containing vinyl monomers; said modified polymers having the following recurring units:



wherein

R₁: a hydrogen atom or lower alkyl groups

R₂: unsaturated groups such as $-\text{CH}=\text{CH}-$, $-\text{C}-$,
 $\begin{array}{c} || \\ \text{CH}_2 \end{array}$

(2—2): a composition consisting of modified polymers defined below with or without vinyl monomers; polymers having carboxyl groups in the side chain, e.g., polymers obtained by polymerizing a composition mainly composed of carboxyl group-containing vinyl monomers, which are modified with glycidyl group-containing vinyl monomers,

(2—3): a composition consisting of modified polymers defined below with or without vinyl monomers; polymers having glycidyl group in the side chain, e.g., polymers obtained by polymerizing a composition mainly composed of glycidyl group-containing monomers, which are modified with α,β -ethylenically unsaturated carboxylic acids,

(3) a composition consisting of polymers defined below with or without vinyl monomers; said polymer being relatively small molecule, saturated or unsaturated polyesters or polyamides having polymerizable unsaturated groups at the terminal where unsaturated carboxylic acid or hydroxyl group containing unsaturated compounds are used as a terminator; or said polymers being relatively small molecule, saturated or unsaturated polyester or polyamides having terminal carboxyl groups, which are modified with glycidyl group-containing vinyl monomers,

(4) vinyl monomers such as methacrylate, acrylate, vinyl acetate, vinyl chloride, styrene, methylenebisacrylamide, diallylphthalate, triallylisocyanurate, trimethylolpropane and trimethacrylate.

Compound mentioned in (1) — (4) above are cross-linked by irradiation.

The term "irradiation", as used herein, means high energy primary radiation and/or secondary radiation resulting from the conversion of electron or other particle energy to neutron or gamma radiation, said energies normally being equivalent to at least 100,000 electron volts. While various types of radiation are suitable for this purpose, such as X-rays, gamma rays and beta rays, the radiation produced by accelerated high energy electrons has been found both convenient and economic and gives satisfactory results.

While there is no upper limit to the electron energy that can be so applied advantageously, the effects desired in the practice of this invention can normally be accomplished without having to go to above 20 million electron volts. Generally, the higher the electron energy used, the greater is the depth of penetration into the massive structure of the materials to be treated. For other types of radiation, such as gamma and X-rays, energies equivalent to the above range of electron volts are desirable.

It is intended that the term "irradiation" include what has been referred to in the prior art as "ionizing radiation" which has been defined as radiation possessing an energy at least sufficient to produce ions or to break chemical bonds and thus includes also radiations such as "ionizing particle radiation" as well as radiations of the type termed "ionizing electromagnetic radiation".

The term "ionizing particle radiation" has been used to designate the emission of electrons or highly accelerated nuclear particles such as protons, neutrons, alpha-particles, deuterons, beta-particles, or their analogs, directed in such a way that the particle is projected into the mass to be irradiated. Charged particles can be accelerated by the aid of voltage gradients by such devices as accelerators with resonance chambers, Van der Graaff generators, betatrons, synchrotrons or cyclotrons. Neutron radiation can be produced by bombarding a selected light metal such as beryllium with high energy positive particles. Particle radiation can also be obtained by the use of an atomic pile, radio-active isotopes or other natural or synthetic radioactive materials.

"Ionizing electromagnetic irradiation" is produced when a metallic target, such as tungsten, is bombarded with electrons of suitable energy. This energy is conferred to the electrons by potential accelerators of over 0.1 million electron volts (mev.). In addition to irradiation of this type, commonly called X-ray radiation, an ionizing electromagnetic radiation suitable for the practice of this invention can be obtained by means of a nuclear reactor (pile) or by the use of natural or synthetic radioactive material, for example, cobalt 60.

Various types of high power electron linear accelerators are commercially available, for example, the ARCO type traveling wave accelerator, Model Mark I, operating at 3 to 10 million electron volts, such as supplied by High Voltage Engineering Corporation, Burlington, Massachusetts, or other types of accelerators as described in U.S. Patent No. 2,763,609 and in British Patent No. 762,953 are satisfactory for the practice of this invention.

An electron beam (0.1—20 M rad/sec of dose rate) can be derived from an electron accelerator (acceleration voltage: 0.1—2 MeV), and applied so that the absorbed dose is 0.1—10 M rad.

An ultraviolet ray having a wave length of from 2000 to 8000 Å, preferably from 3000 to 5000 Å may be used. Preferably a photopolymerization catalyst will be present. The catalyst includes carbonyl compounds such as benzoin, benzoin methyl ether, benzoin isopropyl ether, 2-phenyl thioacetophenone, benzyl, butyroin and anisoin ethyl

ether. It further includes polynuclear quinones such as anthraquinone, chloroanthraquinone, naphthoquinone, and 2-t-butyl anthraquinone, and azo compounds such as azoisobutyronitrile and 2,2'-azobis-2,4-dimethyl valeronitrile. It further includes peroxides such as benzoylperoxide and di-t-butylperoxide, sulphur-containing compounds such as tetramethyl tiuram disulfide and diphenyl disulfide, and halides such as bromo-

form and phenamyl bromide.

The catalyst is preferably used in an amount of from 0.1 to 5% by weight.

The following Examples illustrate the present invention.

Preparation of test pieces

I. Primer coating

A: Galvanized steel plate (Japanese Industrial Standard S 3302, 0.278 m/m thick) treated with zinc phosphate.

B—F: The following isocyanates are coated on A, respectively.

B: Addition product of hexamethylene diisocyanate with water (trade name: Desmodur N—75, Bayer NCO content about 15%), 2—3 μ thick.

C: Addition product of tolylene diisocyanate with water (trade name: Desmodur L—75, Bayer NCO content about 13%), 0.5—1.5 μ thick.

D: Partial addition product of hexamethylene diisocyanate (2 parts) and 50% solution of polyester (hydroxyl value 50) (46 parts); NCO content about 3%, 1—3 μ thick.

E: Hexamethylene diisocyanate (NCO content about 50%), 0.5—1.5 μ thick.

F: Lauryl isocyanate (NCO content 18%), 0.5—1.5 μ thick.

Separately, rolled mild sheet (0.8 m/m thick) is degreased with toluene, and then polished with sand-paper #400 to prepare panel (G).

The panel G is treated as follows: (all parts are referred to parts by weight)

H: A composition containing N-butoxymethyl acrylamide (20 parts), styrene (20 parts), ethyl acrylate (50 parts) and itaconic acid (10 parts) is polymerized. A solution (solid content 50%) is prepared, and the solution (100 parts) is mixed with Desmodur N—75 (34.3 parts). The mixture is applied in 5 μ thick.

I: A mixture of 2-hydroxyethylmethacrylate (10 parts), styrene (20 parts), methacrylonitrile (20 parts) and n-butyl acrylate (50 parts) is polymerized to prepare a 50% solid solution, and the solution (100 parts) is mixed with Desmodur N—75 (22 parts). The mixture is applied in 5 μ thick.

J: Butyral resin (trade mark "Ethlex B") (50 parts) having polymerization degree of 300, butyralization degree of 67 mol %, vinyl alcohol concentration of 28 mol %, is mixed with zinc chromate (70 parts), talc (10 parts), triethanolamine (10 parts) and acetone (1000 parts), and is mixed with an addition product (trade name: Takenate D—11ON) (50 parts) of xylylene diisocyanate (3 mol) and trimethylol propane (1 mol) to prepare a primer solution. Immediately after the mixing, it is coated by a bar coater before a hot air (150° C) is applied for 30 sec. to form a 4 μ thick film.

K: J is repeated except polyester (40 parts) having molecular weight of 1100 and hydroxyl value of 210 obtained by condensing succinic acid (3 mol), diethylene glycol (2 mol) and hexanetriol (2 mol), is used in place of the butyral resin.

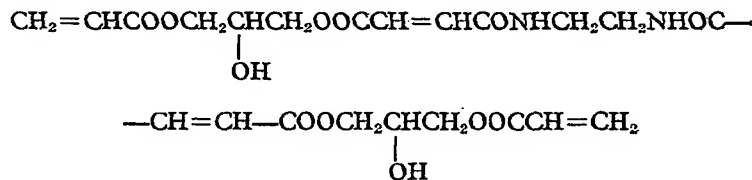
L: K is repeated except polyester having molecular weight of 890 and hydroxyl value of 180 obtained by condensing adipic acid (1 mol), 1,3-butylene glycol (0.8 mol) and trimethylol propane (0.4 mol) is used in place of the polyester.

M: K is repeated except "Takenate D—11ON" (trade name) (35 parts) and polyester (65 parts) are used.

N: A mixture of 2-hydroxyethyl methacrylate (40 parts), n-butyl acrylate (35 parts), styrene (25 parts) is polymerized in toluene (100 parts) to prepare acrylic copolymer having molecular weight of 20,000 and hydroxyl value of 172. To 100 parts of a 50% solution of the acrylic copolymer in toluene is added zinc chromate (72 parts) and talc (10 parts) to prepare a paste. The paste (180 parts) is mixed with "Takenate D—11ON" (50 parts) triethanolamine (10 parts), methylethyl ketone (500 parts) and trichlorethane (500 parts). The mixture is applied by a bar coater, and a hot air (150° C) is applied for 20 sec. to form primer film (4 μ thick).

O: A mixture of 2-hydroxypropyl acrylate (35 parts), ethyl acrylate (40 parts), methyl methacrylate (25 parts) is copolymerized to produce a polymer (molecular weight: 10,000), a 50% solution of the polymer in toluene, and a paste is prepared by mixing the solution (160 parts), zinc chromate (50 parts) and zinc oxide (20 parts). To the paste (150 parts) are added an addition product of hexamethylene diisocyanate and water (trade name: Desmodur N—75, NCO content 15%) (60

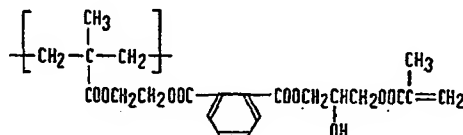
(IV) A mixture of ethylene diamine (12 parts) and maleic anhydride (39 parts) is allowed to react in toluene (100 parts) at 100° C for 1 hour, and then a mixture of glycidyl acrylate (51.2 parts), hydroquinone monomethyl ether (0.3 part) and dimethyl-aminoethyl methacrylate (3 parts) is added thereto. Reaction is conducted for 4 hours to obtain a composition IV comprising the following compound:



(V) A mixture of 2-hydroxyethyl methacrylate (30 parts), methyl methacrylate (20 parts), 2-ethylhexyl acrylate (30 parts), styrene (20 parts), n-dodecyl mercaptane (2 parts) and benzoyl peroxide (2 parts) is polymerized at 98° C for 5 hours to obtain hydroxyl group-containing polymer (molecular weight about 9000).

The polymer (100 parts) is dissolved in a mixture of cyclohexyl methacrylate (100 parts), 2-ethylhexyl acrylate (100 parts) and hydroquinone monomethyl ether (0.2 part), and then phthalic anhydride (30 parts) and dimethyl aminoethyl methacrylate (5 parts) are added thereto. Reaction is conducted at 90° C for 2 hours, and then glycidyl methacrylate (38 parts) is added to proceed the reaction for additional 5 hours.

A composition (V) containing polymers and monomers having units of the following structure: —



(VI) A mixture of ethylene diamine (48 parts), succinic anhydride (40 parts) and toluene (100 parts) is allowed to react at 100° C for 1 hour, and then a mixture of acrylic acid chloride (73 parts), hydroquinone monomethyl ether (0.3 part), dimethyl-aminoethyl methacrylate (3 parts) and pyridine (100 parts) is added. The above mixture is treated for 3 hours at 20° C, and then the following composition (VI) is separated.



(VII) A composition (VII) is made by reacting from a mixture of butyl acrylate (60 parts), methyl methacrylate (17 parts) and ethyl acrylate (15 parts).

Example 1.

A coating composition prepared by adding 2 parts of benzoin isopropyl ether to 100 parts of the composition (I) was coated on the non-treated panel (A) and the isocyanate-treated panels (B) to (E) in a thickness of 100 μ , and was coated with a Mylar (Registered Trade Mark) film to prevent volatilization of the vinyl monomer in the coating composition. The thus obtained film was exposed for 5 min. to the ultraviolet ray using a chemical lamp (20 W; main wavelength; 3600 Å). As the results, the coated films were completely hardened and the Mylar film was removed. The properties of the thus obtained coatings are shown in Table 1.

TABLE 1

Panel plate	A	B	C	D	E	F	G	H	I
Pencil hardness	3H	3-4H	3-4H	4H	3H	3H	4H	4-5H	4-5H
Checker test	40/100	100/100	100/100	100/100	100/100	100/100	20/100	100/100	100/100
Peeling-off test	×	○	○	○	○	○	△	○	○

In Table 1, checker test was conducted in such a manner that 100 squares each having a width of 2 m/m were prepared by cutting the film and thereonto was applied Scotch tape (trade name) to peel off the same. The test result was represented by the number of squares which remained unstripped. Peeling-off test was conducted in such manner that panels were immersed in boiling water for 2 hours and then dried at 60°C for 20 hours. The results obtained were represented by the following marks:

× Coating film was completely peeled off.

△ Coating film was partly peeled off.

○ Coating film was not peeled off.

Example 2.

With each 100 parts of the compositions (II), (III), (IV), (V) and (VII) were mixed 25 parts of rutile-type titanium oxide and 5 parts of Phthalocyanine Green to prepare blue enamels. The thus prepared enamels were coated on the isocyanate-treated panels (B) to (E) and the non-treated panels (A) and (G) in a coating thickness of 20 μ . The thus obtained coating was irradiated using an electron beam accelerator (acceleration voltage: 300 KV; beam current: 25 mA; scanning width: 1 m) in a nitrogen atmosphere at a dose rate of 3 M rad/sec. The properties of the thus treated coating films are shown in Tables 2 and 3.

The Table 2, the panels (A) and (G) are comparative examples. The panels (B), (C), (D) and (E) are those according to the present invention.

From the results in Tables 2 and 3, it is clear that the coatings obtained according to the present invention have good flexibility and adhesion. In addition, the corrosion resistances of the coatings are improved.

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10

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TABLE 2

Composition	(II)							(III)						
	(A)	(G)	(B)	(C)	(D)	(E)	(F)	(A)	(G)	(B)	(C)	(D)	(E)	
Panel plate														
Gloss (%)	78	76	80	85	76	83	76	80	78	81	80	82	83	
Pencil hardness	3H	4H	3H	3H	3H	3H	3H	3H	3H	3H	3H	3H	3H	
Checker test	10/ 100	5/ 100	100/ 100	100/ 100	100/ 100	100/ 100	100/ 100	7/ 100	5/ 100	100/ 100	100/ 100	100/ 100	100/ 100	
Bending property	Peeled off	"	Not changed	"	"	"	"	Peeled off	"	Not changed	"	"	"	
Impact strength	10	10	50	50	45	50	45	10	10	50	50	50	50	
Anti-corrosion	5	8	1	1-2	1-2	1	3	4	8	0	1-2	2	1-2	
Absorbed dose (Mrad)	4	4	4	4	4	4	4	3	3	3	3	3	3	

TABLE 3

Composition	(IV)		(V)			(VII)		
	(A)	(B)	(A)	(C)	(D)	(G)	(H)	(I)
Panel plate								
Absorbed dose (Mrad)	2	2	8	8	8	4	4	4
Gloss (%)	80	82	81	76	79	76	80	79
Pencil hardness	4H	4H	H-2H	H-2H	H-2H	4-5H	5H	5H
Adhesion	70/100	100/100	50/100	100/100	100/100	7/100	100/100	100/100
Bending property	Peeled off	Not changed	Peeled off	Not changed	"	Peeled off	Not changed	"
Impact strength	10	50	20	45	50	10	50	50
Anti-corrosion	3	0	6	1	2-3	Rusty on the whole surface	2-3	2-3

In Tables 2 and 3, the bending property was obtained in such a manner that 1 m/m thick test species was inserted between panels and bended by 180°. The thus bended portion of the coating film was stripped by a Scotch tape. The impact strength was measured according to du Pont's method. The anti-corrosion was shown by the width of rusting after 300 hours spraying aqueous 5% NaCl solution at the cut portion of the coating film.

Example 3.

A paint was prepared by mixing 40 parts of rutile-type titanium oxide with 100 parts of the composition (VI). It was coated on panels (G), (H), (I), (J) and (K) in a coating thickness of 50 μ . The coatings were irradiated using the electron beam accelerator employed in Example 2 at a dose rate of 4 M rad/sec. The properties of the thus treated coatings are shown in Table 4.

TABLE 4

Panel	(G)	(H)	(J)	(I)	(K)
Gloss (%)	85	81	79	78	87
Pencil hardness	H—2H	2H	H—2H	2H	H—2H
Bending test	Peeled off	Not changed	Partly peeled off	Not changed	Partly peeled off
Impact strength	10	50	30	50	30
Anti-corrosion	7—10	0—3	7—10	0—1	7—10
Checker test	20/100	100/100	40/100	100/100	50/100

In Table 4, the bending test was effected under the same conditions as those in Example 2 except that the thickness of the plate inserted between the panels was 3 m/m.

From the results in Table 4, it can be understood that the coatings formed according to the present invention are excellent in the adhesion to the base material, the corrosion resistance and the post-processability.

Example 4.

Desmodur N—75 was coated on to a 0.8 m/m thick aluminum plate, optionally having an Al_2O_3 surface film, to a thickness of 2—3 μ to obtain a coated plate. The composition (III) was coated on to the thus treated plate to a thickness of 30 μ . The coating was irradiated in the same way as in Example 3 so as to obtain a hardened, crosslinked coating. The properties of the thus treated coating are shown in Table 5.

TABLE 5

Panel	Aluminum plate		Aluminum oxide film formed plate	
	Non-treated	Treated	Non-treated	Treated
Isocyanate treatment				
Pencil hardness	3H	3H	3H	3H
Checker test	70/100	100/100	90/100	100/100
Bending test	Peeled off	Not changed	Partly peeled off	Not changed
Impact strength	45	50	45	50
Anti-corrosion	Rust spot by spot	Not changed	Rust spot by spot	Not changed

Example 5.

Desmodur N—75 was coated on a polyester film in a coating thickness of 2 to 3 μ to obtain a pre-treated film. The coating composition prepared by mixing 90 parts of titanium oxide with 100 parts of the composition (A) in Example 2 was coated on the above-obtained pre-treated film in a coating thickness of 20 μ . Electron beams were irradiated on the coating under the same conditions as those in Example 4. It was completely hardened by the irradiation at a dose of 4 M rad.

The adhesion of the thus obtained coating (checker test: 50/100) was remarkably improved in comparison to that of the polyester film, to which the pre-treatment has not been applied (checker test: 0/100).

Example 6.

20 Parts of rutile-type titanium oxide and 7 parts of Phthalocyanine-Blue were mixed with each 100 parts of final painting resin (II), (III), (IV) or (V) to prepare an enamel. This enamel was coated on a non-treated plate (A) and primer-treated plates (B) to (F) in a coating thickness of 20 μ . Electron beams were irradiated on the thus obtained coatings using an electron accelerator (acceleration voltage: 300 KV; beam current: 25 mA) in nitrogen atmosphere at a dose rate of 1.5 M rad/sec. The properties of the thus treated coatings are shown in Tables 6 and 7. In addition, the comparative examples are shown in Table 8. (A)s in Tables (6) and (8) are comparative examples, but they are excellent in processability and corrosion resistance.

In (S) and (U) of Table 7, the crosslinking reaction has proceeded to too much extents so that the peeling off from the final painting film takes place.

In (L') [a comparison to (L)] of Table 6, there are shown an example using a polyester with about 650 molecular weight and 170 hydroxyl value, prepared by condensing 0.2 mole trimethylolpropane, 1.2 mole bisphenol A and 1 mole phthalic acid with a polyester component. The electron beam activity of the top coat resin was lowered due to the protective effect of the aromatic ring in the said polyester component against electron beams. Thus the properties thereof are also deteriorated. (M') of Table 7 [a comparison to (M)] uses 15 parts of (1/2") nitrocellulose, 35 parts of "Takenate D—11ON" (trade name) and 65 parts of polyester. Further (P') of Table 7 shows the example using a resin not containing acrylic esters, prepared in the same way as (P) except that 40 parts of 2-hydroxyethyl methacrylate, 35 parts of n-butyl methacrylate and 25 parts of styrene were used as the polymer component. As the crosslinking, grafting reaction or the like resulting from acrylic esters can not be expected, the properties are deteriorated.

The hardenings by catalyst in Table 8 were carried out by using cobalt naphthenate (1%) and methyl ethyl ketone peroxide (1%) as the catalyst, coating with Mylar film and polymerizing it for 5 hours at 50° C. It can be understood that the electron beam hardenings in Table 8 are far superior to the catalyst hardenings.

Example 7.

Coating compositions prepared by adding 2 parts benzoin methyl ether to each final painting resins (I) and (II) were painted on a non-treated plate and primer-treated plate in a coating thickness of 50 μ , and was coated with Mylar film. Then the coatings were exposed to the irradiation using a high pressure mercury lamp (800 W; length: 50 cm) with 10 cm distance for 3 min. The properties of the thus irradiated coating are shown in Table 9. In peeling off test, when the coating is dipped in boiling water for 2 hours and then dried at 60° C for 2 hours, the complete peeling off of the coating is represented by X; and the non-peeling off is represented by O. From the results in Table 4, it can be understood that the coatings obtained according to the present invention possess excellent properties.

Example 8.

The enamel used in Example 6 was coated on the base materials (V), (W), (X), (Y) and (Z) in a coating thickness of 50 μ . The thus obtained coatings were irradiated with electron beams in the same manner as in Example 6, and were hardened. The properties of the thus hardened coatings are shown in Table 10.

TABLE 6

Final painting	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(II)
Panel plate	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)	(J)	(K)	(L)	(L')	(II)	(II)
Gloss (%)	78	75	76	77	74	76	72	73	74	66	67	78	75		
Pencil hardness	2H	2H	2H	2H	2H	2H	2H	2H	2H	H-2H	H-2H	2H	F-H		
Checker test	0/100	95/100	100/100	100/100	100/100	100/100	5/100	100/100	100/100	95/100	100/100	95/100	95/100		
Bending property	×	○	○	○	○	○	×	○	○	○	○	○	△-○		
Impact strength (cm)	5	35	50	45	45	50	10	50	40	50	50	50	45		
Anti-corrosion (mm)	Whole surface peeled off	4	0	0	1-2	4-5	5	1-3	1-2	1-2	0	1-2	2		
Absorbed dose (Mrad)	3	3	3	3	3	3	3	3	3	3	3	3	3		

TABLE 7

Final painting	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(II)	(III)	(IV)	(IV)	(IV)	(V)	(V)
Plate	(M)	(M')	(N)	(O)	(P)	(P')	(Q)	(A)	(C)	(S)	(R)	(N)	(U)	(T)
Gloss (%)	64	65	74	77	74	74	78	78	77	72	81	79	78	78
Pencil hardness	H—2H	H—2H	2H	2H	2H	2H	2H	2H	2H	3H	3H	3H	H	H
Checker test	90/ 100	95/ 100	100/ 100	100/ 100	100/ 100	95/ 100	100/ 100	0/ 100	100/ 100	0/ 100	95/ 100	100/ 100	100/ 100	100/ 100
Bending property	○	○	○	○	○	○	○	×	○	×	○	○	×	○
Impact strength (cm)	45	50	50	50	45	40	40	5	50	5	40	50	5	50
Anti-corrosion (mm)	1—2	1	0	0	1—2	2	8—10	Whole surface peeled off	0	Whole surface peeled off	1—2	0	Whole surface peeled off	0
Absorbed dose (Mrad)	3	3	3	3	3	3	3	2	2	3	3	3	6	6

TABLE 8

Final painting	(II)	(II)	(II)	(II)
Plate	(E)	(I)	(I')	(E')
Gloss (%)	74	77	67	65
Pencil hardness	2H	2H	H	H
Checker test	100/100	100/100	55/100	45/100
Bending property	○	○	△	△
Impact strength (cm)	45	40	30	25
Anti-corrosion (mm)	1—2	1—2	10 or more	8—9
Absorbed dose (M rad)	3	3	Catalyst hardened	Catalyst hardened

TABLE 9

Final painting	(I)	(I)	(I)	(II)	(II)	(II)
Plate	(A)	(C)	(H)	(A)	(C)	(H)
Pencil hardness	3H	3H	3H	H—2H	H—2H	H—2H
Checker test	0/100	100/100	100/100	0/100	100/100	100/100
Peeling-off test	×	○	○	×	○	○

TABLE 10

Final painting	(III)	(III)	(IV)	(IV)	(IV)
Plate	(V)	(W)	(X)	(Y)	(Z)
Gloss (%)	80	77	78	78	74
Pencil hardness	2H	2H	3H	3H	3H
Checker test	100/100	100/100	100/100	×	100/100
Bending property	○	○	○	△	○
Impact strength (cm)	45	50	40	15	50
Anti-corrosion (mm)	0	1	1—2	Whole surface peeled off	0
Absorbed dose (M rad)	3	3	3	3	3

WHAT WE CLAIM IS:—

1. A process for forming a coating film, which comprises pre-coating the surface of a base material with a first coating material (I) containing 1 to 85 weight % of free isocyanate groups, then coating thereon a second coating material (II) comprising a compound having 0.5 to 12 polymerizable unsaturated groups per 1000 molecular weight units and hardening by crosslinking the thus prepared coating film by irradiation with ionizing radiation and/or ultraviolet ray radiation.
2. A process according to claim 1, wherein a material prepared by partially reacting a polyisocyanate containing 2 or more isocyanate groups per molecule with a compound having a groups reactive with the isocyanate group is used as the coating material (I).
3. A process according to claim 2, wherein the group reactive with the isocyanate group is a hydroxyl group.
4. A process according to claim 2, wherein the group reactive with the isocyanate group is a carboxyl group.
5. A process according to claim 3, wherein the hydroxyl group-containing compound is a butyral resin having 40 mol % or more of butyral units and 60 mol % or less of vinyl alcohol units.
6. A process according to claim 3, wherein the hydroxyl group-containing compound is a polyester having a molecular weight of from 300 to 5000 and hydroxyl value of from 20 to 350 obtained from a polybasic carboxylic acid and a polyhydric alcohol composition containing at least 30% by weight of aliphatic polyhydric alcohol units.
7. A process according to claim 3, wherein the hydroxyl group-containing compound is an acrylic copolymer having a molecular weight of from 1,000 to 100,000 and a hydroxyl value of from 20 to 300 and containing 20 weight % or more of acrylic ester units.
8. A process according to claim 3, wherein the hydroxyl group-containing compound is a polyether having a hydroxyl value of from 20 to 500 and containing 2 or more ether linkages in its molecule.
9. A process according to claim 3, wherein the hydroxyl group-containing compound is 1,2-polybutadiene having a molecular weight of from 300 to 100,000 and a hydroxyl value of from 20 to 500.
10. A process according to any preceding claim, wherein the coating material (I) includes an organic amine and an organometallic compound.
11. A process according to any preceding claim, wherein the coating material (I) includes a pigment.
12. A process for forming a coating film, which comprises coating the surface of a base material with a first coating material (I) having a free isocyanate group content of from 1 to 85 weight %, drying the thus coated layer until the insoluble portion thereof reaches at least 10% by weight (measured in acetone at 25° C); coating thereon a second coating material (II) comprising a compound containing 0.5 to 12 polymerizable unsaturated groups per 1000 molecular weight units, and hardening by cross-linking the thus obtained film by irradiation with ionizing radiation and/or ultraviolet ray radiation.
13. A process according to claim 12, wherein drying is effected by blowing gas at a temperature of from room temperature to 300° C onto the coated surface.
14. A process according to any preceding claim, wherein the base material is a chemically treated metal plate.
15. A process according to claim 14, wherein the metal plate is of iron, aluminum or zinc.
16. A process according to claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.
17. An article when coated by a process according to any preceding claim.

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